To: Allgeier, Steve[Allgeier.Steve@epa.gov]

Cc: binetti, victoria[binetti.victoria@epa.gov]; Travers, David[Travers.David@epa.gov]; Khera,

Rajiv[Khera.Rajiv@epa.gov]; Wisniewski, Patti-Kay[Wisniewski.Patti-Kay@epa.gov]; Hedrick,

Elizabeth[Hedrick.Elizabeth@epa.gov]; Burneson, Eric[Burneson.Eric@epa.gov]

Sent: Thur 1/30/2014 2:12:30 PM

Subject: RE: WV - formaldehyde presence reported in water tests

Steve – Thanks.

In consideration of the chemical structure of MCHM and the information that was provided in the Eastman MSDS we also were wondering if all of the methanol that are part of the structure would be available for chlorine or just the free methanol. I ask because only 1% of the MCHM is free which I think would mean that there would be small amounts methanol available for reaction of chlorine. If all of the methanol are available it might mean more formation?

From: Allgeier, Steve

Sent: Thursday, January 30, 2014 9:01 AM

To: Arguto, William

Cc: binetti, victoria; Travers, David; Khera, Rajiv; Wisniewski, Patti-Kay; Hedrick, Elizabeth; Burneson, Eric

Subject: RE: WV - formaldehyde presence reported in water tests

Bill.

I found only one piece of information to add to that provided by Rajiv and Elizabeth. Aldehydes (including formaldehyde) are highly biodegradable (DiGiano, Singer, Parameswar, and Lecourt; JAWWA, 2001). For this reason, most treatment plants the use ozone (and consequently produce aldehydes) follow ozone treatment with biofiltration, which has been found to be very effective at removing these ozonation byproducts (Weinberg, Glaze, Krasner, and Sclimenti; JAWWA, 1993). The implications of this biodegradability for the fate of formaldehyde in the distribution are less clear. All distribution systems have a biofilm, but it is not a biofiltration process engineered for contaminant removal. In my opinion, biodegredation of formaldehyde would occur in the distribution system, but at a rate slower than occurs in biolifiltration. However, there is much more contact time in a distribution system (hours) compared with a biofilter (10 to 20 minutes).

I did not find anything about treatment of methanol. I suspect that this is due to the fact that methanol is generally not persistent in aqueous environments, nor is it a treatment byproduct. Thus, there has been little motivation to conduct research on treatment of methanol in drinking water.

Steve

From: Burneson, Eric

Sent: Thursday, January 30, 2014 8:24 AM

To: Arguto, William

Cc: Allgeier, Steve; binetti, victoria; Travers, David; Khera, Rajiv Subject: FW: WV - formaldehyde presence reported in water tests

Bill: Rajiv Khera was able to locate some information about formaldehyde formation. See his note below.

From: Khera, Rajiv

Sent: Thursday, January 30, 2014 8:14 AM

To: Burneson, Eric; Regli, Stig; Grubbs, Thomas; Kempic, Jeffrey; Hautman, Dan; Chen, Jimmy

Cc: Miller, Wynne; Carroll, Gregory; Christ, Lisa

Subject: RE: WV - formaldehyde presence reported in water tests

Hi Eric-

According to WHO guidelines for formaldehyde in drinking water, formaldehyde in drinking-water arises mainly from the oxidation of natural organic (humic) matter during ozonation (Glaze et al., 1989) and chlorination (Becher et al., 1992).

Formaldehyde is a by-product of drinking water chlorination at level of 4ug/L and of ozonation at approximately 10ug/L (Krasner et al, 1989, Weinberg et al, 1993). This information was reported in 2009 WRF publication entitled "Occurrence and Formation of Nitrogenous Disinfection By-Products" which is authored by Stuart Krasner, William Mitch and Paul Westerhoff.

Because formaldehyde is commercially manufactured by oxidation of methanol, mainly by metal oxide process involving Fe/Mo catalyst, I am assuming that in potable water supply if methanol were to be present, chlorine should facilitate its oxidation to formaldehyde as either an intermediate or final product. I have no information on its kinetics and/or other sequential or parallel reactions that would consume formaldehyde to form other disinfection by products and likely be more favorable.

Hope this helps. Thanks

Rajiv

From: Burneson, Eric

Sent: Wednesday, January 29, 2014 5:52 PM

To: Regli, Stig; Grubbs, Thomas; Khera, Rajiv; Kempic, Jeffrey; Hautman, Dan; Chen, Jimmy

Cc: Miller, Wynne; Carroll, Gregory; Christ, Lisa

Subject: FW: WV - formaldehyde presence reported in water tests

Can any one tell me if we have any data that indicates chlorine reacts with methanol to form formaldehyde? This relates to the WV spill and your prompt response would be appreciated?

From: Arguto, William

Sent: Wednesday, January 29, 2014 5:20 PM **To:** Burneson, Eric; Allgeier, Steve; binetti, victoria

Subject: Fw: WV - formaldehyde presence reported in water tests

Any info on chlorine oxidizing methanol

From: Caporale, Cynthia

Sent: Wednesday, January 29, 2014 4:52:03 PM

To: Arguto, William

Subject: FW: WV - formaldehyde presence reported in water tests

FYI

From: Warner, Sue

Sent: Wednesday, January 29, 2014 4:50 PM

To: Caporale, Cynthia; R3 ESC-LB **Cc:** Slayton, Joe; Foreman, Fred

Subject: RE: WV - formaldehyde presence reported in water tests

Formaldehyde (also known as methanal) is formed by the oxidation of methanol. Methanol is a component of the crude MCHM. Finished water samples could contain chlorine, an oxidizing agent.

From: Caporale, Cynthia

Sent: Wednesday, January 29, 2014 4:20 PM

To: R3 ESC-LB

Cc: Slayton, Joe; Foreman, Fred

Subject: FW: WV - formaldehyde presence reported in water tests

Formaldehyde has popped up as an issue due to an article that includes a statement from a Marshall University professor indicating detection of formaldehyde in a finished DW sample. We have been requested to provide information on methodology, detection limits and any knowledge we have on possible breakdown components for MCHM or PPh and whether formaldehyde is a potential breakdown product. We have also been asked to find out the method and detection limit used by the University (Thank you Dr. Gundersen for taking that task!).

I would like to have a meeting tomorrow to touch base on where we are with the various analyses of the tank sample and discuss preparation for incoming samples scheduled for later this week. I will send out a meeting invite for 10:30am tomorrow.

For those of you not involved in the actual analysis you are still welcome to attend and share your thoughts and ideas but this meeting is not required.

A big thank you goes to Eric, Jennie, Adam, Sue Warner, Peggy, Robin, Joe, Ron and John for making time this week to expeditiously work on the tank sample. Hopefully I didn't miss anyone.

From: Miller, Linda

Sent: Wednesday, January 29, 2014 3:31 PM

To: Caporale, Cynthia

Subject: FW: WV - formaldehyde presence reported in water tests

From: Miller, Linda

Sent: Wednesday, January 29, 2014 3:30 PM

To: Ferrell, Mark; Burns, Francis; Arguto, William; Wisniewski, Patti-Kay; Hodgkiss, Kathy; Casillas, Laura; Snyder, Raquel; Distefano, Nichole; Capacasa, Jon; Pomponio, John; White, Terri-A; Seneca, Roy; Heron, Donna;

Smith, Bonnie; Forren, John

Subject: RE: WV - formaldehyde presence reported in water tests

Third article has important perspective from Secretary Huffman. Mark - thanks so much for keeping us all on the pulse of things there! Linda

UPDATED: DEP officials unaware of connection between formaldehyde and spill

Marshall professor says 'what we know scares us, and we know there's a lot more we don't know'

by **Dave Boucher**

Daily Mail Capitol Bureau Chief

Advertiser

Updated (2:30 p.m.): The head of the state Department of Environmental Protection questioned a report that formaldehyde found in Charleston tap water is connected to the recent chemical spill.

"We are not aware of formaldehyde being an issue related to the tank spill," DEP Secretary Randy Huffman said Wednesday afternoon.

"Formaldehyde is in a lot of stuff, and so I'm not sure, we're unaware of any relationship...of the formaldehyde to the tanks at Freedom," he said.

"I absolutely don't want to downplay the significance for the potential of formaldehyde in any way."

Earlier Wednesday Dr. Scott Simonton, vice chairman of the West Virginia Environmental Quality Board and a Marshall University professor, told lawmakers he had test results showing formaldehyde in water from a restaurant in downtown Charleston.

At least 10,000 gallons of crude MCHM and PPH spilled from a faulty storage tank owned by Freedom Industries near the Elk River. Officials found the leak Jan. 9, but experts believe it would have taken at least 20 hours for that amount of chemical to leak from the tank.

The results for three different samples taken Jan. 13 at Vandalia Grille show 32 or 33 micrograms per liter of formaldehyde in the water. Simonton said results from many other samples taken from many other places are still being processed.

"It scares me a lot, because it's a known human carcinogen, so any exposure, no matter how slight, is going to increase cancer risks" Simonson said after the legislative meeting.

"Now, that increased risk can be terribly, terribly small. The problem is, we're seeing it in water, we don't know what the concentration is in air."

Huffman questioned the ability for Simonton to connect any formaldehyde at the restaurant to the spill.

"He turned on a spigot, and he measured formaldehyde from a spigot in a restaurant...from a distribution system. It needs to be traced back from there to a potential source," Huffman said.

He explained what he meant later in the interview.

"The way you do that is to start backwards from where you found the material. It may be unique to the restaurant, it may be unique to West Virginia American Water. If it is something that they're getting, that West Virginia American Water is getting in their intake, then certainly we will assist with that," Huffman said.

Once the crude MCHM comes in contact with anything--water, sunlight, skin--it can breakdown, Simonton told lawmakers. One of those products is methanol, and formaldehyde is a product of methanol, he said.

He acknowledged formaldehyde could come from anywhere, but it's very likely these results are directly related to the spill.

"If we go out to the extreme, it could have been put there by martians," Simonton said.

"But the most likely scenario is a breakdown of MCHM."

State and water company officials have only discussed testing for crude MCHM and PPH. Huffman experts need to have an idea of what to test for in order to test for it.

Any further examination regarding formaldehyde in the water falls under the purview of state health officials, he said.

"If they think there's a raw source of formaldehyde in the river or something, that's obviously something we would get engaged in," Huffman said.

"But the breakdown of the chemical when it gets into the water system and whatever it turns into, that would clearly be something that the health department regulates."

A spokeswoman for the state Department of Health and Human Resources did not immediately respond to a request for comment.

Linda Miller

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From: Ferrell, Mark

Sent: Wednesday, January 29, 2014 2:35 PM

To: Burns, Francis; Arguto, William; Wisniewski, Patti-Kay; Hodgkiss, Kathy; Casillas, Laura; Snyder, Raquel; Distefano, Nichole; Capacasa, Jon; Pomponio, John; Miller, Linda; White, Terri-A; Seneca, Roy; Heron, Donna;

Smith, Bonnie; Forren, John

Subject: WV - formaldehyde presence reported in water tests

Time

http://nation.time.com/2014/01/29/west-virginia-official-people-are-inhaling-formaldehyde/

Gazette

http://www.wvgazette.com/News/201401290053

Daily Mail

http://www.charlestondailymail.com/News/201401290055

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